

PREDICTING AROMATICS FORMATION FROM PROPARGYL REACTIONS: DEVELOPMENTS IN AROMATICS-FORMATION MODELING IN THE 1990'S

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ABSTRACT

Predicting the formation of aromatics and soot is a long-sought goal for combustion design, and propargyl (C_3H_3) chemistry appears to be a key. Self-combination reactions and addition to propyne or propadiene have all been proposed to form aromatic rings. Some of these proposals have been based on careful calculations or on clean experimental data. However, the picture is quite complex and in dispute because of the complex rearrangements that can result from chemical activation. Using theory and experiment, I will discuss the controversy over the various proposed kinetics. In the next ten years, we should be able to establish the correct kinetics and use it for engineering analysis and design.

INTRODUCTION

Clean air was one of the central concerns as the environmental movement grew though the 1960's, and sooty air has been one of the worst offenders throughout time. Percival Pott's recognized in the 18th century that combustion-generated soot was linked to cancer, but this insight only led to better personal hygiene requirements for chimney sweeps, not to reduced amounts of soot. Indeed, coal use in the 19th century's Industrial Revolution exacerbated the problem. Reduction began in the 20th century, spurred by an increased scale of industry and increased acceptance of individual rights relative to those industries, and aided by the use of natural gas and new environmental control technologies. A US landmark was the 1970 formation of the Environmental Protection Agency.

Twenty years later, the Clean Air Act of 1990 pushed industry to reduce emissions of smog-forming chemicals, carbon monoxide, and particulates up to $10\text{ }\mu\text{m}$ in size, such as soot. Incentives were mixed with regulation. Subsequent 1997 amendments led to tightening by adding specific standards for particulate matter smaller than $2.5\text{ }\mu\text{m}$.

The US Department of Energy, Department of Defense, and Environmental Protection Agency, as well as government agencies around the world, have long supported research to identify the chemical pathways that form soot. The guiding hypothesis is that by knowing the pathway, it can be interfered with to prevent or destroy soot. Wagner's 1980 review [1] concluded that soot was made of small graphitic domains of polycyclic aromatic hydrocarbons (variously acronyms as PAH, PCA, or PNA). A large body of work, most notably the daring model of Frenklach *et al.* in 1984 [2], pointed to formation of the first aromatic ring as being the rate-determining step for growth toward soot.

Propargyl (linear C_3H_3 , CHCCH_2) has gained wide support as the key precursor to aromatic hydrocarbons in flames, but its dominance, reaction pathway(s), and kinetics are still controversial. This paper examines the competing ideas in the context of recent calculations and data.

BACKGROUND: LITERATURE ON AROMATICS FORMATION

In 1989, Westmoreland *et al.* [3] reviewed the precursors and routes to single-ring aromatics which had been proposed to date. Previous mechanistic proposals had focused on molecular pathways (polyacetylene bridging, Diels-Alder additions), ion-molecule reactions, and radical addition or combination. Modeling their acetylene flame data [3] showed that only the radical routes:

- $n\text{-C}_4\text{H}_5 + \text{C}_2\text{H}_2$ (-CHCHCHCH_2 , route proposed by Cole *et al.* [4]);
- $n\text{-C}_4\text{H}_3 + \text{C}_2\text{H}_2$ (-CHCHCCH , proposed by Stehling *et al.* [5] and by Frenklach *et al.* [2]), and/or
- $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3$ (proposed in the literature by Kern and co-workers [6-7])

could be fast enough, necessarily proceeding by chemically activated isomerizations rather than thermal steps. However, they could not establish which of the three reactant pairs dominated, nor whether the detected C_4H_5 and C_4H_3 were the proper isomers.

Several possible propargyl paths then were proposed around the early 1990's:

- In 1989, we subsequently proposed [8] and later tested [9] a chemically activated pathway from C_3H_3 via chemically activated 1,5-hexadiyne and 1,2,4,5-hexatetraene, isomerizing to 3,4-dimethylenecyclobutene (DMCB). Corresponding thermal isomerizations are recognizable as a Cope rearrangement and a 2+2 sigmatropic ring closure. We proposed that DMCB might isomerize to fulvene (methylenecyclopentadiene) and then to benzene, possibly decomposing to phenyl + H. Chemical activation at the low-pressure (adiabatic) limit could allow reaction above all these intrinsic barriers. Reaching any well would require bimolecular collisions. This hypothesized route was based on thermal pyrolyses of the intermediates. Our reaction modeling [9] implied that phenyl would be an important product at high temperatures.
- Stein and co-workers [10] developed a similar route independently and at about the same time, using their VLPP data and the flame data of Ref. [1]. It proposed that DMCB might isomerize directly either to fulvene or benzene.
- Alkemade and Homann proposed another route [11] involving cyclopropenyl intermediates.
- Miller *et al.* [12] had proposed formation of benzene from propargyl, and Melius, Miller, and Evleth [13] later proposed a variety of routes based on singlet carbene intermediates, BAC-MP4/MP4/6-31G(d,p)/UHF/6-31G(d) potential energy surfaces, and adiabatic RRKM calculations. The end products were phenyl + H.

These promising proposals do not mean that we know that aromatics are formed from propargyl or that we know by what rate. Modeling by Frenklach *et al.* [14] in 1997 implied that the C_4H_3 route might be more important than the C_3H_3 route in some flames and at lower temperatures. Likewise, $C_3H_3+C_3H_4$ is still discussed, and $C_3H_3+C_3H_5$ routes have been proposed and supported by using assumed rate constants in large-mechanism modeling of shock-tube and flame data [15]. Finally, the different possible channels from $C_3H_3+C_3H_3$ will have different pressure dependences. In lieu of clean, direct measurement of rates and products at high temperatures, we must make use of more complex flame data and of calculations.

EXAMINING FLAME DATA

Recent MBMS measurements in an allene-doped ethylene flame by Oulundsen [16] allow comparisons to species in a matching undoped flame of Bhargava and Westmoreland [17]. Although most species are unperturbed, C_3 's and C_6H_6 are affected.

Molecular-beam mass spectrometry (MBMS) was used to measure profiles of free-radical and stable-species mole fractions in one-dimensional flames (Table 1). Both flames had the same fuel-rich equivalence ratio $\phi = 1.90$ (fuel-rich), pressure of 2.666 kPa (20.00 Torr), and velocity at the burner of $u_{b-300} = 62.5$ cm/s. The doped flame was composed of 0.50 % allene, C_2H_4 , O_2 , and 49.7 % Ar, in comparison to the undoped flame with only C_2H_4 , O_2 , and 50.0 % Ar. The profiles were mapped between 0.5 mm and 45.0 mm above the burner surface. Mole fraction profiles were moved 0.9 mm (5 times the orifice diameter) towards the burner surface to account for probe perturbations. The temperature profile and area-expansion ratio were measured in the first study [17].

Calibration uncertainties affect the comparison of profiles. Among the C_3 's, propene (C_3H_6) was calibrated directly, and C_3H_4 in the allene-doped flame was calibrated directly with allene. Other species were calibrated by the method of relative ionization cross-sections, C_3H_2 and C_3H_3 relative to C_3H_4 , and C_3H_5 relative to C_3H_6 , and C_3H_4 in the undoped flame (a mixture of propyne and allene) relative to C_3H_6 . Direct calibration has an uncertainty of <10%, while the indirect calibration should be within a factor of two.

The surprise is that C_3H_3 remains constant within experimental uncertainty (Fig. 1), while C_6H_6 rises more than an order of magnitude ($\times 20$) in the allene-doped flame. C_6H_6 also peaks almost 4 mm earlier than propargyl and 3 mm earlier than its maximum in the undoped flame, which had been almost at the same position as that of propargyl.

Roughly, if propargyl were the sole reactant making benzene higher by a factor of twenty, we would have expected its mole fraction to be higher in the doped flame by a factor of 4-5 (square root of 20), but it is unchanged. A difference in rate of benzene destruction would affect this simple analysis. However, the temperatures and the mole fractions of H, O, and OH hardly change at all, so the oxidative environment for C_6H_6 is unchanged. Another contribution might be $C_3H_3+C_3H_4$ reaction, seeing that C_3H_4 is high and C_3H_3 is unchanged before the peak in C_6H_6 , but the C_3H_4 mole fractions would have to be a factor of twenty higher in this region, and they are not.

A second interesting observation is that mass 41, assigned to C_3H_3 , peaks at the same position as C_6H_6 (Fig. 2). Mass 41 probably has some contribution from HCCO, as mass 42 appears to be dominated by CH_2CO rather than C_3H_6 . However, modeling implies that allyl and 2-propenyl

are formed easily from H+allene, and we propose that CH_2CO is formed from the chemically activated reaction $\text{O}+\text{allene} = \text{H}+\text{CH}_2\text{CO}$.

Table 1. Species measured in low-pressure flat flames of ethene/oxygen/50.0% argon and 0.50% propadiene/ethene/oxygen/49.7% argon at fuel-rich ($\phi=1.90$) conditions.

Species	Ethene	Propadiene/ethene	Species	Ethene	Propadiene/ethene
H	Profile	Profile	CH_2CO	Profile*	Profile
H_2	Profile	Profile	$\text{CH}_2\text{CHO}^{**}$	Profile	Profile
CH_2	Profile	Profile	CH_3CHO	Profile	Profile
CH_3	Profile	Profile	CO_2	Profile	Profile
CH_4	Profile	Profile	C_4H_2	Profile	Profile
OH	Profile	Profile	C_4H_3	-	Profile
H_2O	Profile	Profile	C_4H_4	Profile	Profile
C_2H_2	Profile	Profile	C_4H_5	-	Profile
C_2H_3	Profile	Profile	C_4H_6	-	Profile
C_2H_4	Profile	Profile	$\text{C}_3\text{H}_3\text{O}/\text{C}_4\text{H}_7$	-	Profile
CO	Profile	Profile	$\text{C}_3\text{H}_4\text{O}/\text{C}_4\text{H}_8$	Profile	Profile
HCO	Profile	Profile	$\text{C}_3\text{H}_6\text{O}/\text{C}_4\text{H}_{10}$	Profile	Profile
H_2CO	Profile	Profile	C_3H_4	Profile	Profile
O_2	Profile	Profile	C_3H_6	Profile	Upper bound
HO_2	-	Profile	$\text{C}_4\text{H}_3\text{O}/\text{C}_3\text{H}_7$	Profile	Upper bound
H_2O_2	-	Profile	$\text{C}_4\text{H}_4\text{O}/\text{C}_3\text{H}_8$	Profile	-
C_3H_2	Profile	Profile	$\text{C}_4\text{H}_6\text{O}/\text{C}_3\text{H}_{10}$	Profile	-
C_3H_3	Profile	Profile	$\text{C}_4\text{H}_8\text{O}/\text{C}_3\text{H}_{12}$	Profile	-
C_3H_4	Profile	Profile	C_6H_2	Profile	Profile
Ar	Profile	Profile	C_6H_4	Profile	Profile
HCCO	-	Postflame profile	C_6H_5	Profile	Profile
C_3H_5	Profile	Profile	C_6H_6	Profile	Profile

*Reported previously as C_3H_6 . **Possibly CH_2CHO^+ ionization fragment of CH_3CHO .

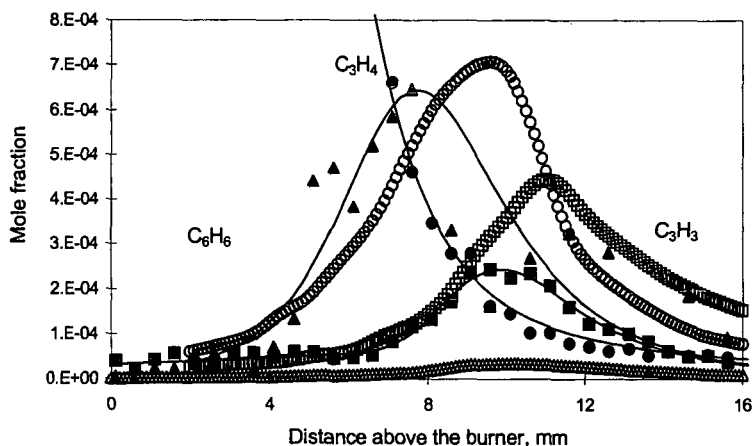


Figure 1. Species profiles in the ethene flames, undoped (open symbols) and allene-doped (filled symbols and lines): C_3H_4 (circles), C_3H_3 (squares) and C_6H_6 (triangles) in ethene flames.

Allyl has long been proposed as a precursor to benzene [18]. Stoichiometry works against it, though; its combination product C_6H_{10} has much hydrogen to lose. Also, it is not cyclic, and the weak allyl-allyl bond donates little energy for subsequent chemically activated reactions of C_6H_{10} .

Other explanations could be that mass 78 might not be benzene or that benzene is a side product formed from phenyl. Ionization potentials are the basis of identification. They match literature values well for benzene and phenyl, although the IP measurement with electron-impact ionization is not so precise as to distinguish them definitively among hydrocarbon isomers. In the allene-doped flame, phenyl reaches its maximum slightly before benzene (Fig. 2). It is a factor of 10 higher and occurs 2.5 mm earlier than in the undoped flame.

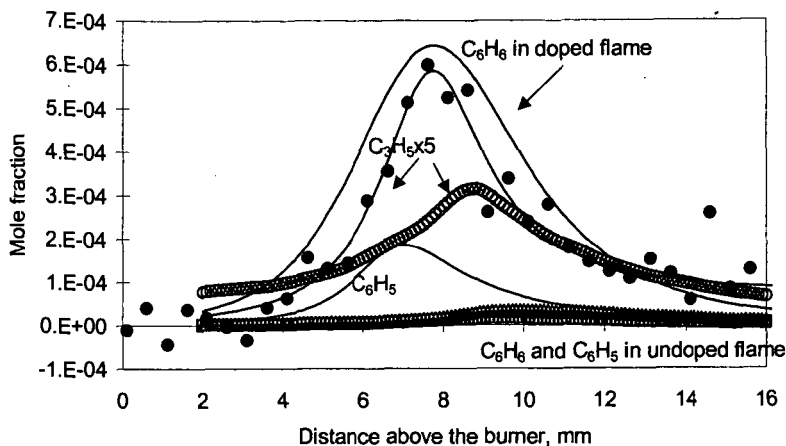


Figure 2. Species profiles in the ethene flames, undoped (open symbols) and allene-doped (filled symbols and lines): C_3H_3 (circles), C_6H_5 (squares), and C_6H_6 (triangles) in ethene flames.

C_4H_3 and C_4H_5 additions to C_2H_2 seem fairly plausible ways to reach aromatics here. Maximum mole fractions occur for C_2H_2 at 9 mm; C_3H_3 at 8.5 mm; C_4H_3 at about 9.5 mm; and C_4H_5 at 7 mm. All these are in the neighborhood of the C_6H_6 maximum. The C_4 radical peaks are both an order of magnitude higher in the doped flame.

CONCLUSIONS

There is strong evidence in many systems that propargyl combination is an important route to forming single-ring aromatics. It does not appear to explain the changes in benzene formation comparing MBMS profiles in a fuel-rich ethane flame with those in a near-identical flame doped with a small amount of allene. In the allene-doped flame, C_4H_3 and C_4H_5 routes may be dominant, despite the potential of allene as a C_3H_3 precursor.

With the correct kinetics, likely to be worked out in the next ten years, we will be able to use soot prediction from flame modeling for engineering analysis and design. To predict soot formation, we must be able to model flames of all sorts of fuels. There is no reason to think that propargyl combination should be the sole route to make aromatics, although it may often be the dominant one. Modeling of these and other flames will be used as an aid to interpreting the roles of the different routes, and new approaches are being applied to tighten the uncertainty of calibration factors.

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